

**For the paragraph at page 7, lines 12-16, please revise as follows:**

In one embodiment, the adsorbent is characterized by preferential adsorption of gaseous alkene from a gaseous mixture comprising the alkene, and the adsorbent comprises: a salt of silver supported on a carrier. The preferred salt is silver nitrate. Other salts of silver are as per the group defined above, where the preferred halide is fluoride.

*[Extra spaces were removed before "fluoride" in line 16 of the above-mentioned paragraph.]*

**For the paragraph at page 7, lines 21-25, please revise as follows:**

The carriers are refractory inorganic oxide, molecular sieve, and activated carbon. The carriers are preferably characterized by a BET surface area greater than about 50 square meters per gram and up to about 2,000 square meters per gram and comprise a plurality of pores having size greater than about 3 angstroms and up to about 10 microns.

**For the paragraph at page 10, lines 26-31, please revise as follows:**

The hydrocarbons used as the adsorbates were ethane (CP grade, Matheson minimum purity 99.0%), ethylene (CP grade, Matheson minimum purity 99.5%), propane (CP grade, Matheson minimum purity 99.0%), and propylene (CP grade, Matheson minimum purity 99.0%); and helium. Helium (pre-purified grade, Metro Welding 99.995%) was used as the carrier gas and as the regeneration gas. The gases were used without further purification.

**For the paragraph at page 14, line 26, through page 15, line 4, please revise as follows:**

In this example, the effect of various anions on olefin adsorption are is shown. By understanding this effect, the adsorptive properties of sorbents are maximized for olefin/paraffin separation. The sorbents were prepared by dispersing silver halides on silica gel via thermal monolayer dispersion. Incipient wetness impregnation was not used due to lack of good solvents. The halides used were AgF, AgCl, AgBr, and AgI. The silver halide content of each sorbent was maintained at around 1.0 mmol/g to facilitate comparison. The sorbents were prepared by mixing the metal halide and the silica gel with thorough mixing. The resulting mixture was heated in air at 350°C for 4 days to

assure proper spreading. The BET surface areas of the resulting sorbents are shown in Table B.

**For the paragraph at page 17, lines 12-20, please revise as follows:**

Examples 1 to 3 show new and more effective sorbents for ethane\ethylene and propane\propylene separations that were synthesized by dispersing AgNO<sub>3</sub> salt over several substrates ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and MCM-41) using incipient wetness impregnation technique. The capacities and selectivities of these new sorbents are significantly better than any known  $\pi$ -complexation sorbents. Adsorption rates for these sorbents were fast with 100% completion achieved within 300 seconds at 25°C. These characteristics make the sorbents most promising for use with pressure swing adsorption processes (PSA), which is described in the examples which follow later (Yang, 1987).

**For the paragraph at page 18, lines 15-21, please revise as follows:**

The effectiveness of these silver salt compounds was further compared to other adsorbents. Three sorbents were used in the following examples; two were commercial sorbents, (4A zeolite and carbon molecular sieve) and one was a  $\pi$ -complexation sorbent of the invention described above (AgNO<sub>3</sub>/SiO<sub>2</sub>) (AgNO<sub>3</sub>/SiO<sub>2</sub>). The comparison was based on modelling modeling a PSA cycle, representative of a commercial use of such adsorbents. Equilibrium isotherms, heats of adsorption, and temperature-dependent diffusivities diffusivities were measured for four gases on three sorbents.

**For the paragraph at page 19, lines 1-10, please revise as follows:**

The  $\pi$ -complexation sorbent used in this work was prepared using thermal monolayer dispersion to disperse AgNO<sub>3</sub> over an SiO<sub>2</sub> substrate. The sorbent was prepared by mixing 0.32 grams of AgNO<sub>3</sub> (Stem Chemicals) per gram of SiO<sub>2</sub> (Stem Chemicals). The SiO<sub>2</sub> had a surface area of 670 m<sup>2</sup>/g and a pore volume of 0.46cm<sup>3</sup>/g. The particle size of the SiO<sub>2</sub> utilized ranged from 100 to 200 mesh. After thorough mixing, the sample was heated in air at 200°C for 89 h to assure complete dispersion. The BET surface area of the sorbent was measured at 384 m<sup>2</sup>/g by nitrogen adsorption at 77 K. Pore size was calculated to be 23 Å using the BJH method described in detail by

Barrett, et al. (1951). Other  $\text{AgNO}_3/\text{SiO}_2$  ratios were also used; the ratio just given yielded the best results.

**For the paragraph at page 19, lines 11-22, please revise as follows:**

Equilibrium isotherms, uptake curves, and surface-area measurements were made utilizing a Micromeritics ASAP 2010 adsorption instrument and a Shimadzu TGA-50 thermogravimetric analyzer. The ASAP 2010 utilizes a volumetric system to obtain adsorption isotherms and uptake curves. All uptake curves were measured at a stepped pressure increment from 0 atm to 0.1 atm. Also, measurements were made at various temperatures to obtain isosteric heat of adsorption data and the temperature dependence of diffusivities diffusivities. Surface-area measurements were carried out by nitrogen adsorption at 77 K. The hydrocarbons used were: ethane (CP grade, Matheson minimum purity 99.0%), ethylene (CP grade, Matheson minimum purity 99.5%), propane (CP grade, Matheson minimum purity 99.0%), and propylene (CP grade, Matheson minimum purity 99.0%). The gases were used without further purification.

**For the paragraph at page 20, lines 4-15, please revise as follows:**

The objective of this example was to compare the performance of the adsorbents employing equilibrium separations, kinetic separation, and separation by exclusion of one of the components. The comparison needed to be carried out using nearly identical cycle conditions. In the case of ethane/ethylene ethane\ethylene separation, the adsorbents were compared at the same product throughput and the product purity was studied at various product recoveries. In the case of propane/propylene propane\propylene separation, the adsorbents had highly differing productivities, and hence the comparison was done at constant product purity and the product throughput was studied at various values of product recovery. It should be noted that the term "product" mentioned throughout this work refers to the olefin-rich product obtained in desorption step 4 unless otherwise specified. The various process variables in this work were defined as follows:

Product recovery is as defined in equation 1.

Purge-to-feed ratio (P/F) is as defined in equation 2.

Another important parameter used to gauge the adsorbent's productivity is the product throughput (also referred to as productivity in this work):

Production throughput is as per equation 3.

**For the paragraph at page 21, line 27, through page 22, line 4, please revise as follows:**

For adsorption by  ~~$\pi$ -complexation~~  $\pi$ -complexation, the equation giving the most satisfactory fit to experimental data has been known to be the Langmuir-uniform-distribution (LUD) equation (Yang and Kikkinides, 1995; Chen and Yang, 1995). Both the physisorption and chemisorption terms were included in the isotherm. At present, however, no equation is available for its extension to multicomponent mixtures. Hence, the loading ratio correlation (LRC) extended to binary mixtures was used (Yang, 1987) as per equation 11, where  $q_m$ ,  $b$  and  $n$  were LRC parameters. The temperature dependence of  $q_m$  and  $b$  was given as per equation 12.

**In the paragraph heading at page 22, line 16, please delete “Diffusitives” and insert --Diffusivities--.**

**For the paragraph at page 22, line 22, through page 23, line 3, please revise as follows:**

Uptake rates were measured using Micromeritics ASAP 2010 at 25 °C and 70 °C, and the results are shown in Fig. 10. The pressure increments were from 0 atm to 0.1 atm. At 25 °C, after 15 s, C<sub>2</sub>H<sub>4</sub> adsorption was approximately 75% complete, while C<sub>2</sub>H<sub>6</sub> adsorption was only 15% complete. Diffusion time constants,  $D/R^2$ , were calculated by fitting experimental data with the solution for the diffusion equation for spherical particles (Kärger and Ruthven, 1992). The values of  $D/R^2$  obtained for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> at 25 °C were  $5.12 \times 10^{-3}$  and  $1.64 \times 10^{-4}$ , L/s<sup>1</sup>, respectively. The ratio of these ~~diffusivities~~ diffusivities was 31, which was similar to the ratio of pure-component ~~diffusivities~~ diffusivities of O<sub>2</sub>/N<sub>2</sub> in the commercial separation of air using a carbon molecular sieve. However, it was observed that the desorption rate of the C<sub>2</sub>H<sub>4</sub> on zeolite

4A was low compared to that of adsorption rate, thus giving it an irreversible nature. Unlike C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> adsorption was completely reversible at this temperature.

**In the paragraph heading at page 23, line 19, please delete “Diffusitives” and insert --Diffusivities--.**

**For the paragraph at page 23, lines 20-25, please revise as follows:**

Unlike the 4A zeolite with a discrete aperture dimension, the CMS had a distribution of micropore sizes ranging from 3 Å to 5 Å. Measurements with C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> showed that these molecules were totally excluded. The equilibrium isotherms of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>8</sub> at various temperatures are shown in Fig. 13. C<sub>2</sub>H<sub>6</sub> was nearly excluded, yet detectable amounts were observed due to the larger pores in the CMS.

**For the paragraph at page 25, line 7, through page 26, line 3, please revise as follows:**

The performance of the sorbents needed to be compared by keeping one of the following three parameters ~~constant~~ constant: product purity, product recovery, and product throughput. As comparable product throughputs were obtained in the case of zeolite 4A and the Ag<sup>+</sup>-Amberlyst-35, comparison was done by studying the product purity vs. product recovery at an average product throughput of about  $1.1 \times 10^4$  kg product/h/kg adsorbent. The PSA cycle conditions used in the simulation runs are given in Table 4 and the results of the simulations are shown in Fig. 15. The dots in the figure represent actual results of the simulation runs, while the line indicates the trend followed. As can be seen from the figure, the C<sub>2</sub>H<sub>4</sub> product purity fell rapidly at high C<sub>2</sub>H<sub>4</sub> product recovery for both the sorbents at constant productivity. High recovery was possible at low product purities, but it fell drastically at very high purity in the case of zeolite 4A. However, in the case of Ag<sup>+</sup>-Amberlyst-35 resin sorbent, much higher C<sub>2</sub>H<sub>4</sub> product recovery was possible compared to zeolite 4A at corresponding product purity and at the constant product throughput under consideration. Although, in general, the runs for Ag<sup>+</sup>-resin show a slightly lower product throughput than that for zeolite 4A, comparison

between runs 1 and 2 for  $\text{Ag}^+$ -resin and runs 6 and 7 for zeolite 4A in Table 4 is valid, since product throughputs are about the same for both. Hence, it can be concluded that equilibrium separation by  $\pi$ -complexation adsorbents such as  $\text{Ag}^+$ -Amberlyst-35 gives better performance than kinetic separation using zeolite 4A. Moreover, both curves in Fig. 15 could be raised by further lowering the product throughput. Although product purities in excess of 99.9% were possible for the  $\text{Ag}^+$ -resin at recoveries lower than 10%, the product throughput dropped further. Hence these data could not be shown in this figure. The monolayer  $\text{AgNO}_3/\text{SiO}_2$  sorbent of the invention has selectivity for ethylene similar to that of  $\text{Ag}^+$ -resin and in addition has much higher diffusivities compared to the latter sorbent. Hence the disadvantage of having low product throughputs for  $\text{Ag}^+$ -resin can be overcome by using the  $\text{AgNO}_3/\text{SiO}_2$  sorbent with negligible diffusion limitation.

**For the paragraph at page 26, line 30, through page 27, line 8, please revise as follows:**

For the case of propane/propylene, the adsorbents that were considered for separation were zeolite 4A and monolayer  $\text{AgNO}_3/\text{SiO}_2$ . Zeolite 4A almost excludes propane from its pores, as can be seen from Fig. 11, and hence makes it an excellent prospect for  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  separation. The  $\text{AgNO}_3/\text{SiO}_2$  adsorbent of the invention possesses a good selectivity, steep isotherm, and hence a large working capacity for  $\text{C}_3\text{H}_6$  compared to that for  $\text{C}_3\text{H}_8$ . Thus this sorbent, which employs equilibrium separation due to  $\pi$ -complexation, is also a good candidate for this separation. The Bergbau-Forschung CMS adsorbent was found to exclude both  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$  from its pores, and hence it was not considered for this olefin/paraffin system.

**For the paragraph at page 29, line 18, through page 30, line 8, please revise as follows:**

A similar type of behavior was observed with change in purge velocity. As before, when the initial temperatures of the bed were altered from 70°C to 120°C, the system displayed multiple steady states for a range of purge velocities. Fig. 19 displays the transient product purity profiles as the system approaches cycle steady state for adsorption pressure of 1 atm, desorption pressure of 0.1 atm, feed temperature of 70°C,

step of 210 s, time constant ( $t_s$ ) of 50 s, feed velocity of 0.80 m/s, and purge velocity ranging from 0.18 m/s to 0.19 m/s. The approach to a middle unstable state and then its bifurcation to upper and lower stable steady states seen in **Fig. 19** was similar to that in **Fig. 17**. The effect of the interstitial purge velocity on the  $C_3H_6$  product concentration starting from two different initial temperatures is shown in **Fig. 20**. The lower branch in the figure represents the product purities obtained when the bed was started with an initial temperature of 70°C. As the purge velocity was increased from 0.186 m/s to 0.187 m/s, the product purity suddenly increased to 98.4% from 80%. The upper branch was obtained by starting with an initial temperature of 120°C, and a similar jump was seen at 0.184 m/s. Thus for the small range of purge velocities between 0.184 m/s and 0.186 m/s, multiple steady states were observed with respect to the initial temperature of the bed. A further study of the effect of initial temperature on the product-purity dependence of feed and purge velocity in the region of multiplicity revealed that all simulations carried out at initial temperatures below 106°C followed the behavior observed for the initial temperature of 70°C, whereas all initial temperatures above 107°C gave the behavior observed for the that of 120°C.